Stabilization of sulfenyl(poly)selenide ions in *N*,*N*-dimethylacetamide

Abdelkader Ahrika, Julie Robert, Meriem Anouti and Jacky Paris*

Laboratoire de Physicochimie des Interfaces et des Milieux Réactionnels, UFR Sciences et Techniques, Parc de Grandmont, 37200, Tours, France. E-mail: paris@univ-tours.fr

Received (in Montpellier, France) 16th January 2002, Accepted 27th May 2002
First published as an Advance Article on the web 5th September 2002

Whereas redox processes resulted from the reactions $PhSe^-/S_8$ or $PhSe_2Ph/S_3^{\bullet -}$, mixed anions $RSSe_y^-$ ($R = Ph, PhCH_2$; $y = 1$–3) were obtained by the slow addition of solid selenium to thiolate ions in *N*,*N*-dimethylacetamide. The $RS^- + n$ Se reactions, which were investigated by spectroelectrochemistry, led initially ($n = 1$) only to the formation of $RSSe^-$ ions. These species oxidized into RS_2R faster than RS^- on a gold electrode, with the simultaneous electrodeposition of very reactive microcrystals of selenium. On a preparative scale, the substitution of $RSSe^-$ ions ($R = CH_3$, Ph) on alkyl halides yielded $RSSeR'$ compounds ($R' = PhCH_2$, CH_3, respectively) which greatly disproportionated. Further additions of Se ($n = 2$, 3) to RS^- ions led to $RSSe_2^-$ and $RSSe_3^-$ in equilibrium with RS_2R and mixtures of Se_x^{2-} polyselenide ions ($x = 4,6$; 6,8). Visible spectra of $RSSe_2^-$ and $RSSe_3^-$ ions were calculated from the study of the backward reactions $RS_2R + Se_x^{2-}$ ($x = 4$, 6).

We previously reported that solid selenium slowly reacts with RSe^- selenolate ions in *N*,*N*-dimethylacetamide (DMA), a dipolar aprotic medium, yielding successively RSe_y^- ions [eqn. (1); R = Ph, $PhCH_2$; $y = 2$–4].[1] RSe_3^- and RSe_4^- ions disproportionate [eqn. (2)] into diselanes and Se_x^{2-} polyselenide ions which had been characterized ($x = 4$, 6, 8):[2]

$$RSe^- + (y-1)\ Se(s) \rightarrow RSe_y^- \quad (1)$$

$$2\ RSe_y^- \rightleftharpoons RSe_2R + Se_x^{2-} \quad (2)$$

Reactions (1) are similar to those observed between sulfur and thiolates leading to RS_y^- ions (R = alkyl, $y = 2$–5).[3] However, very little is known about 'mixed anions' such as $RSSe_y^-$ or $RSeS_y^-$ ($y \geqslant 1$): a variety of selenenyl thiolates ($RSeS^-Li^+$) resulting from the addition of one sulfur unit to lithium alkyl selenolates (RSe^-Li^+) in THF were characterized *in situ* by ^{77}Se NMR at 193 K;[4] however 'RSeS$^-$ readily underwent internal redox-reactions below room temperature' [eqn. (3)], and $RS^- + Se$ (or Te) processes were described as ineffective in THF.[4]

$$2\ RSeS^- \rightarrow RSe_2R + S_2^{2-} \quad (3)$$

Using UV-visible absorption spectrophotometry, we recently showed that the stoichiometric addition of sulfur to selenolate ions $2\text{-}NO_2C_6H_4Se^-$ ($ArSe^-$, $\lambda_{max} = 520$ nm; $[S]_{ad}/[ArSe^-]_0 = 1$) yielded ≃85% of $ArSeS^-$ ions ($\lambda_{max} = 728$ nm);[5] these species being partly oxidized in the presence of excess sulfur [eqn. (5)]:[5]

$$2\ ArSe^- + S_2 \rightleftharpoons 2\ ArSeS^- \quad (4)$$

$$2\ ArSeS^- + 3\ S_2 \rightleftharpoons Ar_2Se_2 + S_8^{2-} \quad (5)$$

While the formation of $ArSe_2^-$ as in eqn. (4) ($ArSe^- + Se$) was complete, the conversion of ArS^- into $ArSSe^-$ only reached 20%.[5]

It has now been established that RS_2^- ions oxidize into RS_2R faster than RS^- ions on a gold electrode, according to eqns. (6) and (7):[3,6]

$$2\ RS^- + S_2 \rightleftharpoons 2\ RS_2^- \quad (6)$$

$$2\ RS_2^- - 2\ e^- \rightarrow RS_2R + S_2 \quad (7)$$

Surprisingly, analogous anodic behaviours have been reported with RSe_2^-[1] and $ArSSe^-$ species,[5] suggesting fast heterogeneous reactions between RSe^- or ArS^- ions and electrogenerated solid selenium. This hypothesis is reconsidered in the present paper which is mainly devoted to the expected stabilization of $RSSe_y^-$ ($y \geqslant 1$; R = Ph, $PhCH_2$) and $PhSeS^-$ ions. The reactions RS^-/Se and $PhSe^-/S$, RS_2R/Se_x^{2-} ($x = 4$, 6, 8) and $PhSe_2Ph/S_3^{\bullet -}$ were therefore followed by UV-visible spectrophotometry coupled with voltammetry (CV and rotating gold disc electrode). Natural selenium-containing compounds have been the subject of extensive studies because of their possible cancer chemopreventive properties.[7,8] 'Selenenyl sulfides' $RSeR'$ identified in *Allium* volatiles from speciation experiments,[9] are most frequently prepared by reactions between thiols (RSH) and selenenyl halides ($R'SeX$, X = Br, Cl).[10] These species are also obtained by mixing the symmetrical products RS_2R and $R'Se_2R'$ of the usual disproportionation (8):[11]

$$2\ RSeR' \rightleftharpoons RS_2R + R'Se_2R' \quad (8)$$

Our spectroelectrochemical results on the stabilization of $RSSe^-$ ions were then applied on a preparative scale, to two typical alkylations of RS^- (R = CH_3, Ph) + Se solutions.

Results and discussion

S_x^{2-}, Se_x^{2-}, RS^- and RSe^- ions in DMA

There is now general agreement concerning the nature of polysulfide ions in dipolar aprotic media.[12,13] In *N*,*N*-dimethylacetamide, sulfur reduces in two bielectronic steps with respect to S_8 on a gold rotating electrode [waves R_1 and R_2, $E_{1/2}(R_1) = -0.40$ V *vs.* reference, $E_{1/2}(R_2) = -1.10$ V].[13] The electrolysis at controlled potential on the plateau of R_1 occurs *via* the disproportionation (9) of red S_8^{2-} ions ($\lambda_{max1} = 515$ nm, $\varepsilon^8_{515} = 3800$ dm^3 mol^{-1} cm^{-1}; $\lambda_{max2} = 360$ nm, $\varepsilon^8_{360} = 9000$ dm^3 mol^{-1} cm^{-1}), up to the stable blue $S_3^{\bullet -}$ radical-anion ($\lambda_{max} = 617$ nm, $\varepsilon^3_{617} = 4100$ dm^3 mol^{-1} cm^{-1}) in equilibrium with its dimer S_6^{2-} in a minor proportion. In our opinion cyclooctasulfur is in equilibrium with the reactive S_2 molecules, thus appearing in equations such as (9).[13]

Table 1 Redox processes occuring at a Se-coated gold disc electrode in DMA and related peak potentials *vs.* reference Ag/AgCl, KCl sat. in DMA–NEt_4ClO_4 (0.1 mol dm^{-3}) from CV at a scan rate of 100 mV s^{-1}

Redox process	Peaks[a] (potential/V)	
$8Se_{(s)} + 2e^- \rightleftharpoons Se_8^{2-}$	R_1 (−0.49)	O_1' (−0.33)
$3Se_8^{2-} + 2e^- \rightleftharpoons 4Se_6^{2-}$	R_2 (−0.62)	O_1' (−0.33)
$2Se_6^{2-} + 2e^- \rightleftharpoons 3Se_4^{2-}$	R_3 (−0.89)	O_2' (−0.65)
$3Se_4^{2-} + 2e^- \rightleftharpoons 4Se_3^{2-}$(?)	R_4 (−1.28)	O_3' (−1.0)
$2Se_3^{2-} + 2e^- \rightarrow 3Se_2^{2-}$(?)	R_5 (−1.55)	

[a] R = cathodic; O = anodic.

Table 2 Electrochemical and spectrophotometric characteristics of RY_2R and RY^- species (Y = Se, S) in DMA—$E_{1/2}$ at a rotating gold disc electrode *vs.* reference

	RY_2R	RY^-		
R, Y	$E_{1/2}$(R)/V	$E_{1/2}$(O)/V	λ_{max}/nm	ε_{max}[a]
Ph, Se	−0.76	−0.36	318	12 700
Ph, S	−1.25	+0.02	309	18 200
$PhCH_2$, S	−1.55	−0.03	285[b]	3850

[a] ε_i/dm^3 mol^{-1} cm^{-1}. [b] Shoulder.

$$S_8^{2-} \rightleftharpoons 2\ S_3^{\bullet -} + S_2 \quad (9)$$

$$3\ S_8 + 8\ e^- \rightarrow 8\ S_3^{\bullet -} \quad (10)$$

S_8^{2-} and $S^{-1/3}$ ions ($S_3^{\bullet -} \rightleftharpoons S_6^{2-}$) oxidize ($O_1$) and reduce ($R_2$) at the same potentials [$E_{1/2}(O_1) = -0.20$ V; $E_{1/2}(R_2) = -1.10$ V].

Prior to this study, Se_x^{2-} ions (x = 8,6,4) were successively obtained by coulometric reduction (R_1–R_3 steps) of weighed amounts of grey selenium coating a large gold grid electrode.[2] Two further reduction steps detected on cyclic voltammograms (R_4, R_5, perhaps leading to Se_3^{2-} and Se_2^{2-} as in liquid ammonia)[14] were not identifiable by our method because of passivation phenomena on the gold electrode surface. The redox processes summarized in Table 1 and the known UV-visible spectra[2] providing molar absorbance of the stable Se_x^{2-} ions (Fig. 1; x = 8, λ_{max} = 648, 453, 398 nm; x = 6, λ_{max} = 598, 440 nm; x = 4, λ_{max} = 550, 417 nm) were used for quantitative data processing in this study.

RY^- ions (Y = Se, R = Ph; Y = S, R = Ph, $PhCH_2$) were generated ([$RY^-]_0 \leqslant 4 \times 10^{-3}$ mol dm^{-3}) by electrolysis of RY_2R species at a controlled potential of a gold electrode on the plateau of their bielectronic waves (Y = Se,[1,15] Y = S[3,16]) according to previously described procedures [eqn. 11f]:

$$RY_2R + 2\ e^- \underset{b}{\overset{f}{\rightleftharpoons}} 2\ RY^- \quad (11)$$

The electrochemical and spectrophotometric characteristics of RY_2R and RY^- species are summarized in Table 2.

$PhSe_2Ph/S_3^{\bullet -}$ and $PhSe^-/S_8$ reactions

The addition of $PhSe_2Ph$ to $S_3^{\bullet -}$ ions resulted in instantaneous changes in voltammograms and spectra (Fig. 2) which agreed with equilibrium (12):

$$PhSe_2Ph + 8\ S_3^{\bullet -} \rightleftharpoons 2\ PhSe^- + 3\ S_8^{2-} \quad (12)$$

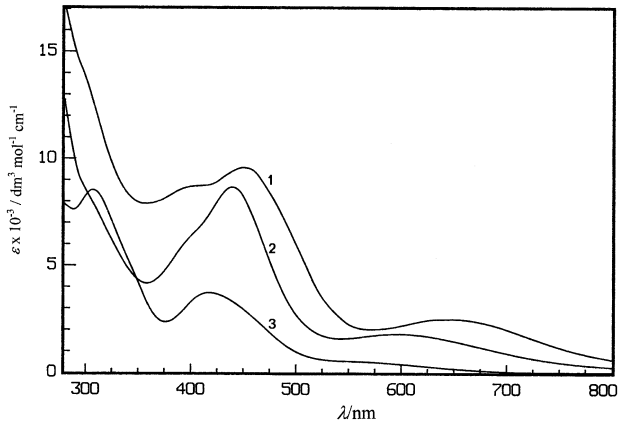

Fig. 1 UV-visible absorption spectra (ε_i/dm^3 mol^{-1} cm^{-1}) of Se_8^{2-} (1), Se_6^{2-} (2) and Se_4^{2-} (3) ions in dimethylacetamide.

$A_{617}(S_3^{\bullet -})$ decreased in favor of A_{515} (S_8^{2-} and A_{360} (S_8^{2-}, and $PhSe^-$ in part) according to calculated $\Delta[S_3^{\bullet -}]/\Delta[S_8^{2-}]$ values close to $-2.6 \simeq -8/3$, and through the same isosbestic point (λ_{is} = 545 nm) as in the course of electrooxidation (13) of $S^{-1/3}$ ions:[13]

$$8\ S_3^{\bullet -} \rightarrow 3\ S_8^{2-} + 2\ e^- \quad (13)$$

However, as shown by the growth of the reduction wave of $PhSe_2Ph$ [$E_{1/2}$(R) = −0.76 V] from the first additions of diphenyl diselenide, preceding the constant cathodic current of $S_3^{\bullet -}$/S_8^{2-} ions [$E_{1/2}$(R) = −1.10 V] reaction (12) was not quantitative. At the stoichiometric value $[PhSe_2Ph]_{ad}/[S_3^{\bullet -}]_0 = 1/8$ in the experimental conditions of Fig. 2, consumption of $S^{-1/3}$ ions only reached 40%. S_8^{2-} ions remained unreactive towards $PhSe_2Ph$ since A_{515} always increased with addition of the substrate in excess. Conversely, sulfur quantitatively reacted with benzene selenolate ions in accordance with eqn. (14):

$$2\ PhSe^- + S_8 \rightarrow PhSe_2Ph + S_8^{2-} \quad (14)$$

With the addition of sulfur to $PhSe^-$ ions the spectra were the same as those observed when S_8 was electrolyzed at 2 F mol^{-1} S_8 for various $[S_8]_0$ concentrations,[13] regardless of $[S]_{ad}/[PhSe^-]_0$ ratio values between 0 and 1: the increases of absorbances at 515 nm (S_8^{2-}) and 617 nm ($S_3^{\bullet -}$) because of the partial disproportionation (9) with a negligible sulfur proportion always confirmed (±6%) the conservation eqn. (15):

$$[S_8]_0 = [S_8^{2-}] + 1/2[S_3^{\bullet -}] \quad (15)$$

At the same time, the reduction currents of $PhSe_2Ph$ [$E_{1/2}$(R) = −0.76 V] and of $S_3^{\bullet -}/S_8^{2-}$ ions [$E_{1/2}$(R) = −1.10 V] increased, while the anodic wave of the latter [$E_{1/2}$(O) = −0.20 V] progressively replaced that of $PhSe^-$ ions [$E_{1/2}$(O) = −0.36 V] up to stoichiometry (14).

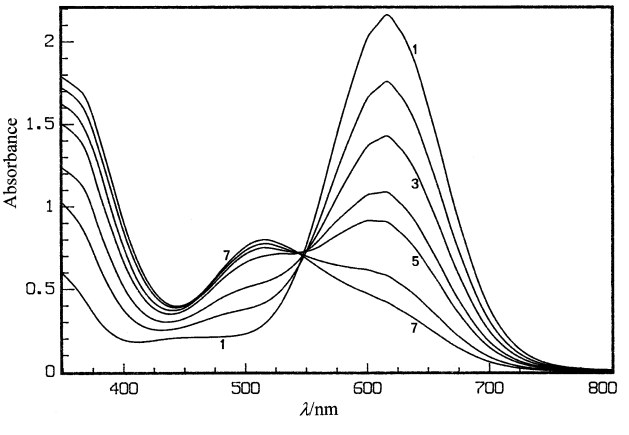

Fig. 2 Dependence of the UV-visible spectra on the addition of diphenyl diselenide to a $[S_3^{\bullet -}]_0 = 6.06 \times 10^{-3}$ mol dm^{-3} solution. $[PhSe_2Ph]_{ad}/[S_3^{\bullet -}]_0$ = 0 (1); 0.063 (2); 0.12_5 (3); 0.23 (4); 0.32 (5); 0.50_3 (6); 0.96 (7). Thickness of the cell = 0.1 cm; scan rate = 500 nm min^{-1}.

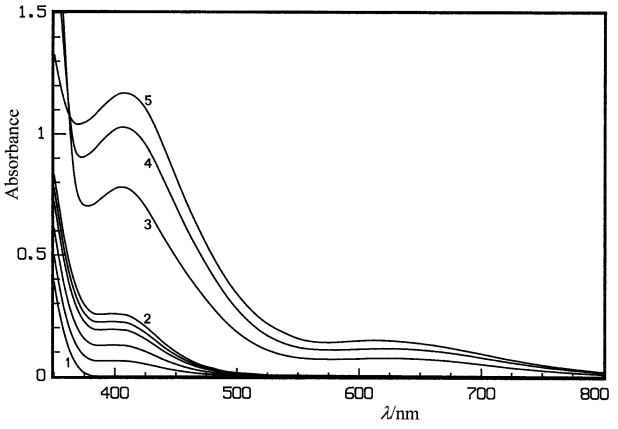

Fig. 3 Changes in UV-visible spectra with the addition of selenium powder to a $[PhS^-]_0 = 2.87 \times 10^{-3}$ mol dm^{-3} solution. $n = (Se)_{ad}/(RS^-)_0 = 0$ (1); 0.99 (2); 1.98 (3); 2.99 (4); 4.0 (5); recordings at equilibrium except for (1) → (2), $A = f(t)$, $0 < t < 95$ min.

Thus, in contrast to the two successive steps which were evidenced in the course of the addition of sulfur to the least reducing 2-$NO_2C_6H_4Se^-$ ($ArSe^-$) species,[5] formation (4) of $ArSeS^-$, then reversible oxidation (5) into $ArSe_2Ar$, only redox processes (12) and (14) resulted from the reactions $PhSe_2Ph/S_3^{\bullet -}$ and $PhSe^-/S_8$, respectively, without any observed stabilization of $PhSeS^-$ ions.

Stabilization and electrocatalytic oxidation of $RSSe^-$ ions

When grey selenium powder (pellets, diameter *ca.* 10–30 μm) was added to stirred solutions of PhS^- and $PhCH_2S^-$ ions at a ratio $n = (Se)_{ad}/(RS^-)_0 = 1$, the changes in UV-visible spectra and cyclic voltammograms were similar in both cases, as illustrated in Figs. 3 and 4 (R = Ph). In the course of the Se consumption which required about 1.5 h up to $n = 1$, two absorption bands regularly increased with time: R = Ph (see Fig. 3, curves 1 → 2), $\lambda_{max1} = 403$ nm, $\lambda_{max2} = 260$ nm, isosbestic point $\lambda_{is} = 272$ nm; R = $PhCH_2$, $\lambda_{max1} = 430$ nm, $\lambda_{max2} = 260$ nm, $\lambda_{is1} = 324$ nm, $\lambda_{is2} = 298$ nm), in agreement with the formation of only $RSSe^-$ ions:

$$RS^- + Se(s) \rightarrow RSSe^- \qquad (16)$$

As soon as solid Se was added, and before any growth of absorbance at about 400 nm, the oxidation current of RS^- ions into RS_2R [Fig. 4, curve 1, $Ep^a = +0.04$ V, $Ep^c = -1.40$ -1.40 V] totally shifted towards less anodic potentials (curve 2, $Ep^a = -0.37$ V). At the end of reaction (16) $PhSSe^-$ had an oxidation peak at -0.44 V (curve 3), and reversal of the voltage scan direction resulted in the appearance of the sharp reduction peak of electrodeposited Se [$Ep^c(1) = -0.49$ V][2] followed by the subsequent cathodic peaks 2–5 of the polyselenide ions (Table 1), then associated anodic peaks (3′, 2′). This electrochemical behavior of RS^- ions in the presence of selenium complies with the following electrocatalytic mechanism [eqns. (16)–(18)], which is analogous to those previously reported for RS^-/RS_2^-[3,6] and RSe^-/RSe_2^- species:[1]

$$2\ RS^- - 2e^- \rightarrow RS_2R \qquad (17)$$

$$RS^- + Se(s) \rightarrow RSSe^- \qquad (16)$$

$$2\ RSSe^- - 2e^- \rightarrow RS_2R + 2\ Se(s) \qquad (18)$$

Thus, RS_2^-, RSe_2^- and $RSSe^-$ ions oxidize into RY_2R (Y = S, Se) on a gold electrode, at a greater rate than RY^- ions, as shown by the differences between their respective half-wave potentials of oxidation listed in Table 3. The occurrence of the catalytic processes from the addition of insoluble selenium to RY^- ions (Y = S, Se) implies fast heterogeneous reactions such as in eqn. (16) between RY^- and the released Se in the course of electrooxidation [*e.g.*, eqn. (18)], although RSe_2^- or $RSSe^-$ were only obtained by direct addition (1) or (16) after 1.5 hour. The same schemes were tested on quantitative electrolysis at a controlled potential of a large gold grid electrode ($E = -0.10$ V), of a solution containing $ArSe^-$ [Ar = 2-NO_2Ph, $E_{1/2}(O) = +0.16$ V, $\lambda_{max} = 520$ nm, $\varepsilon_{max} = 1200$ dm^3 mol^{-1} cm^{-1}][5] and $ArSe_2^-$ [$E_{1/2}(O) = -0.25$ V, $\lambda_{max} = 728$ nm, $\varepsilon_{max} = 3450$ dm^3 mol^{-1} cm^{-1}][5] ions: $[ArSe^-]_0 = 3.40 \times 10^{-3}$ mol dm^{-3}, $[ArSe_2^-]_0 = 2.25 \times 10^{-3}$ mol dm^{-3} [spectral changes in Fig. 5 as a function of z F mol^{-1} $(ArSe^-)_0 + (ArSe_2^-)_0$]. As long as $ArSe^-$ ions were in greater

Table 3 $\Delta E_{1/2}(O)$/V variation of anodic half-wave potentials[a] related to the oxidations of RYZ^- and RY^- ions into RY_2R species

	R = Ph	R = $PhCH_2$	R = Ar[b]
Y, Z = S,S	−0.23	−0.46	−0.50
Y, Z = Se,Se	−0.08	−0.06	−0.41
Y, Z = S,Se	−0.47	−0.35	−0.68

[a] $\Delta E_{1/2}(O) = E_{1/2}(RYZ^-) - E_{1/2}(RY^-)$. [b] Ar = 2-$NO_2C_6H_4$.

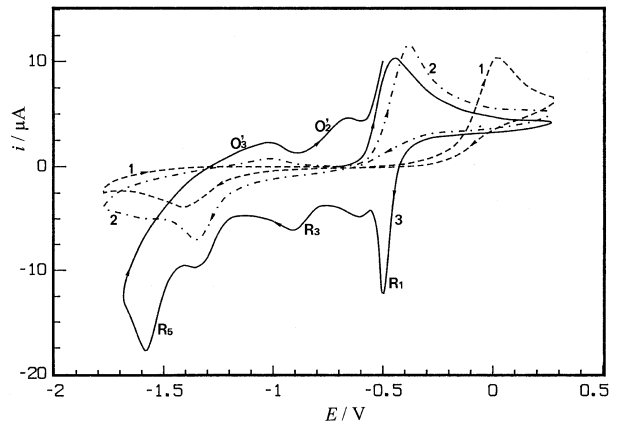

Fig. 4 Cyclic voltammograms of a $[PhS^-]_0 = 3.52 \times 10^{-3}$ mol dm^{-3} (0.14 mmol) solution (1) added with selenium powder (11 mg, 0.14 mmol); $\Delta t = 2$ min (2); 92 min (3). *E vs.* Ag/AgCl, KCl sat. in DMA–NEt_4ClO_4 0.1 mol dm^{-3}. Scan rate = 50 mV s^{-1}.

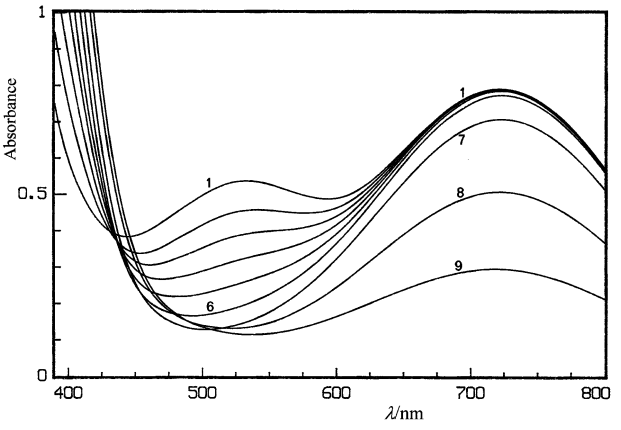

Fig. 5 Spectral changes in the course of the electrooxidation at $E = -0.10$ V *vs.* reference of a $[ArSe^-]_0 = 3.40 \times 10^{-3}$ mol dm^{-3} + $[ArSe_2^-]_0 = 2.25 \times 10^{-3}$ mol dm^{-3} solution (Ar = 2-NO_2Ph): z F mol^{-1} $(ArSe^-)_0 + (ArSe_2^-)_0 = 0$ (1)–0.58 (6); 0.65 (7); 0.75 (8); 0.85 (9).

concentration than initially added Se ($[ArSe^-] > [ArSe_2^-]_0$, $z < 0.60$, curves 1–6), the decrease in A_{520} was in accordance with the oxidation of $ArSe^-$ ions into $ArSe_2Ar$ (growth of its cathodic wave, $E_{1/2} = -0.69$ V)[5] at a potential ($E = -0.10$ V) only suited to that of $ArSe_2^-$ [eqn. (19)]:

$$2\ ArSe_2^- - 2\ e^- \rightarrow ArSe_2Ar + 2\ Se(s) \qquad (19)$$

Simultaneously A_{728} ($ArSe_2^-$) remained at a constant value because of the 'instantaneous' reaction between $ArSe^-$ and Se which was generated at the electrode surface. Then ($z > 0.60$), curves 7–9), the consumption of $ArSe_2^-$ (decrease in A_{728}) resulted in the deposition of solid selenium on the gold grid, and the recovery of $ArSe_2Ar$ ($z \simeq 1.05$) according to its characteristic absorption at 378 nm ($\varepsilon_{max} = 7300$ dm^3 mol^{-1} cm^{-1}).[5]

Similarly, a gold foil (1 × 1 cm) was coated with grey selenium by electrolysis ($E = -0.25$ V) of $PhSSe^-$ ions (about 0.076 mmol), and then observed by scanning electron microscopy (SEM). The SEM images shown in Figs. 6a–6b revealed an epicentric crystallization with small dendrites, mostly 1 to 2 μm in length, which could explain the high reactivity of 'Se-nucleophiles' such as RY^- species (Y = S, Se) towards electrogenerated selenium.

The recent interest in biochemistry of RSSeR′ species[7–9] led us to examine the alkylation of two $RSSe^-$ solutions on a preparative scale as examples: $CH_3SSe^- + PhCH_2Br$ and $PhSSe^- + CH_3I$. The compositions of the mixtures of products RSSeR′, RS_2R, $R'Se_2R'$ which were analyzed by ^{1}H NMR and GC/MS (see Experimental) corresponded to significant disproportionation of the expected selenenyl sulfides CH_3SSeCH_2Ph (≃80%) and $PhSSeCH_3$ (≃70%), as previously reported for this class of rather unstable compounds [eqn. (8)].[11]

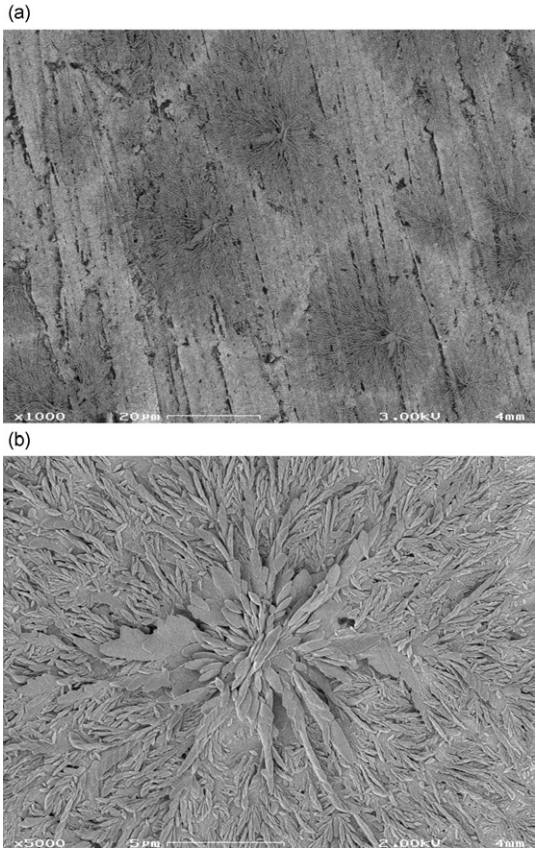

Fig. 6 Scanning electron micrographs of electrodeposited selenium on a gold foil from the oxidation of $PhSSe^-$ ions ($E = -0.25$ V). (*a*) ×1000; (*b*) ×5000.

Formation of $RSSe_y^-$ ions

Further additions of solid selenium to $RSSe^-$ ions [R = Ph, $PhCH_2$, $n = (Se)_{ad}/(RSe^-)_0$ greater than 1] resulted in its total consumption within 2 h ($n = 2$), then 2.5 h ($n = 3$), whereas traces of solid Se remained unreactive for $n = 4$ beyond 4 h. The partial oxidation of the anionic solutions was shown by the appearance of Se_x^{2-} ions ($x \geqslant 4$). Mixtures of these species were detected by the simultaneous increase in their absorption at around 625 nm (Se_6^{2-}/Se_8^{2-}, R = Ph, Fig. 3, curves 3–5) or 590–620 nm (Se_4^{2-}/Se_6^{2-} or Se_6^{2-}/Se_8^{2-}, R = $PhCH_2$), and in their reduction waves (RDE, $x = 8, 6, 4$; $E_{1/2} = -0.55, -0.83, -1.20$ V),[2] with greater currents at potentials close to those of RS_2R (R = Ph, $E_{1/2} \simeq -1.25$ V; R = $PhCH_2$, $E_{1/2} \simeq -1.55$ V). At the same time another absorption band increased at about 405 nm (R = Ph) or 380 nm (R = $PhCH_2$) which could not be related to Se_x^{2-} ions from the shape of their own spectra (Fig. 1). Moreover, spectra and voltammograms were the same when equilibrium was attained for the respective stoichiometries: $RS^- + 2$ Se (R = Ph, Fig. 3, curve 3) and $RS_2R + Se_4^{2-}$; $RS^- + 3$ Se (Fig. 3, curve 4) and $RS_2R + Se_6^{2-}$ (see below Fig. 7, curve 5). All of these observations were analogous to those occurring in the course of the $RSe^- + n$ Se(s) ($n \geqslant 2$) and $RSe_2R + Se_x^{2-}$ ($x = 4, 6$) reactions, which yielded RSe_y^- ions ($y = 3, 4$, maximal absorbances at 400–420 nm) in equilibrium with RSe_2R and mixtures of polyselenide ions [eqn. (2)].[1] Here again, the fast reactions $RS_2R + Se_x^{2-}$ (R = Ph, $PhCH_2$; $x = 4, 6$) were followed by calculations first of the polyselenide concentrations as a function of $m = [RS_2R]_{ad}/[Se_x^{2-}]_0$: $[Se_6^{2-}]$ and $[Se_8^{2-}]$ ($598 < \lambda_{max} < 648$ nm), or $[Se_4^{2-}]$ and $[Se_6^{2-}]$ ($550 < \lambda_{max} < 598$ nm), were deduced from experimental values of A_{598} and A_{648} or A_{598} and A_{550}, respectively, by the use of the known ε_i molar absorptivity (Fig. 1), *e.g.* eqn. (20), ε_i (dm^3 mol^{-1} cm^{-1}, ±4%): $\varepsilon^6_{598} = 1750$, $\varepsilon^8_{598} = 2150$;$\varepsilon^8_{648} = 2500$, $\varepsilon^6_{648} = 1450$.[1]

$$A_i = \varepsilon_i(Se_6^{2-})[Se_6^{2-}] + \varepsilon_i(Se_8^{2-})[Se_8^{2-}] \qquad (20)$$

The other concentrations $[RS_2R]$ and $[RSSe_y^-]$, as well as the average number $\bar{y}$ of Se units in $RSSe_y^-$ chains, were then calculated by solving the conservation equations from $[RS_2R]_{ad}$ and $[Se_x^{2-}]_0$ values. As an example, Fig. 7 shows the changes in spectra for the reaction $PhS_2Ph + Se_6^{2-}$. Two steps can be distinguished:

(i) for $0 < m \leqslant 0.42$ (curves 1–2), the maximal absorbance of Se_6^{2-} ions (A_{440}, A_{598}) evolved towards that of Se_8^{2-} (A_{398}, A_{453}, A_{648}) through three isosbestic points ($\lambda_{is} = 398$, 474 and 545 nm), according to the rough stoichiometry of eqn. (21):

$$PhS_2Ph + 2.4\ Se_6^{2-} \rightarrow 2\ PhSSe_{1.6}^- + 1.4\ Se_8^{2-} \qquad (21)$$

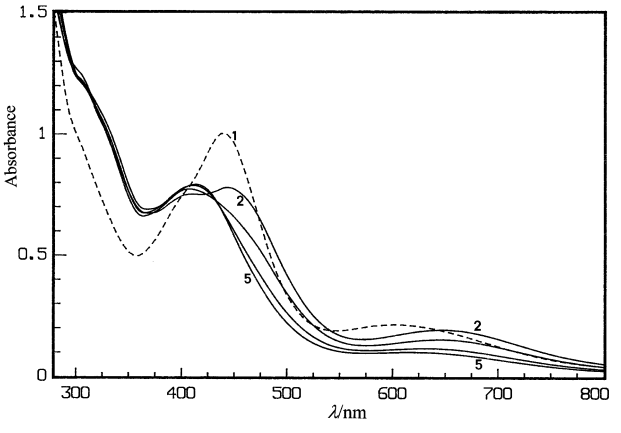

Fig. 7 Changes in UV-visible spectra with the addition of diphenyl disulfide to a $[Se_6^{2-}]_0 = 1.15 \times 10^{-3}$ mol dm^{-3} solution: $m = [RS_2R]_{ad}/[Se_6^{2-}]_0 = 0$ (1); 0.42 (2); 0.66 (3); 0.90 (4); 1.02 (5).

Table 4 Calculated compositions of solutions at equilibrium for the reactions $RS_2R + Se_x^{2-}$ ($x = 4, 6$) and $RS^- + n$ Se ($n = 2, 3$) depending on initial conditions[a]

Initial cond.[a]	$[Se_4^{2-}]$	$[Se_6^{2-}]$	$[Se_8^{2-}]$	$[(RS)_2]$	$[(RSSe_y^-)]$	$\bar{y}$
$[(PhS)_2]_0 = 2.70 + [Se_4^{2-}]_0 = 2.74$	—	0.42	0.21	0.60	4.20	1.6
$[PhS^-]_0 = 2.87 + [Se]_0 = 5.70$	—	0.23	0.15	0.38	2.11	1.5
$[(PhS)_2]_0 = 1.12 + [Se_6^{2-}]_0 = 1.10$	—	0.35	0.17	0.54	1.16	2.7
$[PhS^-]_0 = 2.87 + [Se]_0 = 8.58$	—	0.37	0.22	0.59	1.69	2.7
$[(PhCH_2S)_2]_0 = 2.54 + [Se_4^{2-}]_0 = 2.66$	0.54	0.22	—	0.64	3.80	1.9
$[PhCH_2S^-]_0 = 2.90 + [Se]_0 = 5.70$	0.40_5	0.105	—	0.51	1.88	1.8_5
$[(PhCH_2S)_2]_0 = 1.59 + [Se_6^{2-}]_0 = 1.54$	—	0.47_5	0.20	0.72	1.74	2.7_5
$[PhCH_2S^-]_0 = 2.90 + [Se]_0 = 8.60$	—	0.44_5	0.22_5	0.67	1.56	2.6_5

[a] All concentrations are in mmol dm^{-3}.

(ii) for $0.42 < m \leqslant 1.0$ (curves 2–5), the progressive displacement $A_{648} \rightarrow A_{618}$ agreed with a partial recovery of Se_6^{2-} ions, and with the formation at the same time of $RSSe_y^-$ ions of higher $\bar{y}$ rank (Table 4, $m = 1$, $\bar{y} = 2.7$), giving a maximum absorbance at about 412 nm. These results can be explained by eqns. (22)–(24):

$$RS_2R + Se_6^{2-} \leftrightharpoons 2\ RSSe_3^- \quad (22)$$

$$2\ RSSe_3^- + Se_6^{2-} \underset{b}{\overset{f}{\rightleftharpoons}} 2\ RSSe_2^- + Se_8^{2-} \quad (23)$$

$$2\ RSSe_2^- + Se_6^{2-} \underset{b}{\overset{f}{\rightleftharpoons}} 2\ RSSe^- + Se_8^{2-} \quad (24)$$

In the presence of Se_6^{2-} ions in excess ($m < 0.42$), reactions (22) and (23) totally shift to the right, leading to a mixture of $RSSe^-$ and $RSSe_2^-$ ions by equilibrium (24) ($\bar{y} \simeq 1.6$). With further additions of RS_2R, the consumption of Se_6^{2-} displaces equilibria (23) and (24) in reverse, increasing the $\bar{y}$ value to 2.7 (mixture $RSSe_2^-/RSSe_3^-$).

Similarly, three steps were observed from progressive changes in $A = f(\lambda)$ curves during the addition of PhS_2Ph to the more reducing Se_4^{2-} ions: *(i)* $0 < m \leqslant 0.35$, $A_{550} \rightarrow A_{598}$ and $A_{417} \rightarrow A_{440}$, and thus $Se_4^{2-} \rightarrow Se_6^{2-}$ according to the nearly quantitative redox process (25).

$$PhS_2Ph + 3\ Se_4^{2-} \rightarrow 2\ PhS^- + 2\ Se_6^{2-} \quad (25)$$

(ii) $0.35 < m \leqslant 0.67$, $A_{598} \rightarrow A_{645}$ and $A_{440} \rightarrow A_{450}/A_{400}$ due to further reaction of Se_6^{2-} ions which provided Se_8^{2-} ions in accordance with the overall eqn. (26).

$$PhS_2Ph + 1.5\ Se_4^{2-} \rightarrow 2\ PhSSe^- + 0.5\ Se_8^{2-} \quad (26)$$

(iii) $0.67 < m < 1.0_2$, $A_{645} \rightarrow A_{615}$ and $A_{450}/A_{400} \rightarrow A_{407}$; the reactions of Se_6^{2-}/Se_8^{2-} ions finally led to $\bar{y} \simeq 1.6$ ($m = 1$) by 'Se-exchanges' as in eqn. (24).

The calculated concentrations and average $\bar{y}$ numbers at the end of slow reactions $[RS^-]_0 + n\ (Se)_{ad}$ (R = Ph, $PhCH_2$; $n = 2$, 3) and of the equivalent fast reactions $[RS_2R]_0 + [Se_x^{2-}]_0$ ($m = 1$; $x = 4$, 6) are given in Table 4. Based on $[RS_2R]$ values at equilibrium compared with $[RS^-]_0$ or $[RS_2R]_0$ (Table 4, R = Ph and $PhCH_2$), the disproportionations of $RSSe_y^-$ ions could therefore be roughly situated at *ca.* 25% ($y = 2$) and 45% ($y = 3$). These levels meet those of RSe_3^- (30%) andRSe_4^- (~45%) ions [eqn. (2)].[1] Furthermore, the spectra of $RSSe_y^-$ ions ($y = 2$, 3) were obtained over the wavelength range 350–600 nm as previously obtained for RSe_3^- and RSe_4^- ions:[1] *(i)* $RSSe^-/RSSe_2^-$ and $RSSe_2^-/RSSe_3^-$ mixtures were assumed to give $1 < \bar{y} < 2$ and $2 < \bar{y} < 3$ respectively, with definite compositions linked to $\bar{y}$ values (*e.g.* $\bar{y} = 1.6$, 40% $RSSe^-$ and 60% $RSSe_2^-$); *(ii)* for the most accurate conditions $[RS_2R]_0 = [Se_x^{2-}]_0$, the absorbances of Se_x^{2-} ions ($x = 6$, 8 or 4, 6) calculated by the use of concentrations in Table 4 and characteristics in Fig. 1 were subtracted from the experimental A values, 10 nm apart; *(iii)* the known spectra of $RSSe^-$ ions ($RS^- + 1$ Se, $\varepsilon_i \pm 5\%$) led firstly to those of $RSSe_2^-$ ($x = 4$), then $RSSe_3^-$ ($x = 6$). The $A = f(\lambda)$ curves are reported in Fig. 8 for R = Ph, whereas Table 5 summarizes the spectrophotometric characteristics of $RSSe_y^-$ ions (R = Ph, $PhCH_2$; $y = 1$–3). λ_{max} wavelengths of $RSSe_y^-$ ions were lower by $\simeq$25 nm than those of homologous $RSeSe_y^-$ species ($y = 1$–3), with close ε_y values in both cases.[1] The formation of $RSSe_4^-$ ions could not be proved from the addition of RS_2R disulfides to Se_8^{2-} ions, because of the detection of solid selenium within the solutions in the course of the reactions which entailed at first the shift A_{648} (Se_8^{2-}) $\rightarrow A_{630}$ (Se_8^{2-}/Se_6^{2-}).

Conclusions

Whereas selenolate ions undergo redox exchanges to RSe_2R diselenides with sulfur in *N*,*N*-dimethylacetamide, selenium adds to thiolates with the formation of the sulfur–selenium bond in $RSSe^-$ species. The latter reactions, and those leading to RSe_2^- ($RSe^- + Se$) which we recently reported, are analogous to the well known 'S-nucleophilic processes' affording RS_2^- ions from thiolates and sulfur.

In mixtures $RS^- + RSSe^-$, $RSSe^-$ ions oxidize into RS_2R faster than RS^- ions on a gold electrode, with a fast heterogeneous reaction between selenolate ions and electrogenerated selenium. RSSeR′ alkylated selenenyl sulfides disproportionate to a large extent into symmetrical RS_2R and $R'Se_2R'$ compounds.

$RSSe_y^-$ ions ($y = 2$, 3), which partly disproportionate into RS_2R and Se_x^{2-} ions, result from the slow addition of solid Se to $RSSe^-$ ions. The same equilibria are readily obtained by the reactions between RS_2R and Se_x^{2-} ions.

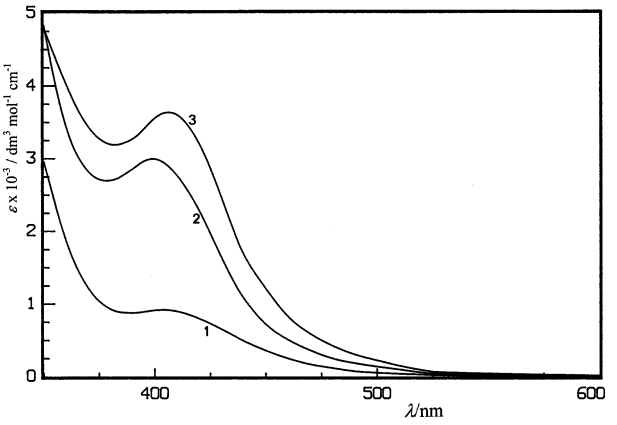

Fig. 8 Calculated spectra (ε_i/dm^3 mol^{-1} cm^{-1}) of $PhSSe_y^-$ ions. $y = 1$–3, (1)–(3).

Table 5 Spectrophotometric characteristics of $RSSe_y^-$ ions ($y = 1$–3) in dimethylacetamide

R		$RSSe^-$	$RSSe_2^-$	$RSSe_3^-$
Ph	λ_{max} [a]/nm	403	400	405
	ε_{max} [b c]	900	3000	3600
$PhCH_2$	λ_{max} [a]/nm	430	375	375
	ε_{max} [b c]	400	2600	3000

[a] $\lambda_{max}(y = 2, 3) \pm 4$ nm. [b] ε_i/dm^3 mol^{-1} cm^{-1}. [c] $\varepsilon_i(y = 2, 3) \pm 15\%$.

Experimental

Materials and equipment

N,*N*-Dimethylacetamide, grey selenium (99.999%, 100 mesh), and all the organic compounds were purchased from Aldrich except for diphenyl diselenide and dibenzyl mono-and di-selenide (Acros Organics). Solvent purification and storage after addition of NEt_4ClO_4 (Fluka, 0.1 mol dm^{-3}) as supporting electrolyte have been reported elsewhere.[17] Spectroelectrochemical equipments and electrodes,[1] as well as the thermostatted (20.0 ± 0.50 °C) flow-through cell[17] have previously been described. All the potentials were referenced to Ag/AgCl, KCl saturated in DMA–NEt_4ClO_4 (0.1 mol dm^{-3}) electrode. The Se-coated gold foil was observed by Scanning Electron Microscopy (SEM FEG Gemini 982 Leo Microscope). The micrographs were obtained in secondary electron image mode (accelerating voltage of 2 kV). The synthesized mixtures were analyzed by ^{1}H NMR spectroscopy (200.132 MHz, Bruker AC 200) with $CDCl_3$ as the solvent (Me_4 Si as standard) and GC-MS (Hewlett-Packard 5989 A, EI 70 eV).

Generation of Se_x^{2-} ions

Accurate concentrations of Se_x^{2-} ions were obtained by the same method as recently reported:[1,2] selenium was initially deposited on a large gold grid electrode [$25 < w(Se)/mg < 40$] by the electrooxidation ($E = 0.0$ V) of Se_x^{2-} solutions ($\bar{x} \simeq 6$) which were themselves chemically generated in DMA from the reduction of Se with hydrazine and sodium methoxide:[18]

$$12\ Se(s) + 4\ MeO^- + N_2H_4 \rightarrow 2\ Se_6^{2-} + 4\ MeOH + N_2 \quad (27)$$

The cathodic polarization of the Se-coated grid in DMA (40 cm^3) was then kept until the spectra and the related maximal absorbances of Se_x^{2-} (Fig. 1; $x = 8$, $E = -0.55$ V; $x = 6$, $E = -0.75$ V; $x = 4$, $E = -1.10$ V) were attained. Concentrated solutions of RS_2R substrates in DMA (R = Ph, $PhCH_2$; $v_{max} = 4$ cm^3) were progressively added to Se_x^{2-} ions. In all cases, absorbances reached equilibrium within 1 min.

Syntheses of RSSeR′ compounds

The $CH_3SSe^- + PhCH_2Br$ and $PhSSe^- + CH_3I$ reactions were carried out according to the same procedure on a preparative scale: solid sodium thiomethoxide (95%) and lithium thiophenoxide (1 mol dm^{-3} in THF) of commercial origin were dissolved in 80 cm^3 of deaerated DMA under an N_2 atmosphere. The RS^- solutions were stirred at 50 °C with selenium powder ($Se:RS^- = 1:1$) which reacted within 3 hours. Stoichiometric amounts of alkyl halides dissolved in DMA (20 cm^3) were then added dropwise (20 min) at room temperature to the yellow $RSSe^-$ solutions. After filtration (0 °C) of the medium and addition of water (300 cm^3), the products were extracted with diethyl ether. The organic phase was thoroughly washed with water (elimination of residual DMA) and dried over $MgSO_4$. After evaporation *in vacuo*, the mixtures were rapidly analyzed without attempting to separate the individual compounds because of the poor stability of the RSSeR′ species.[10,11]

Reaction of CH_3SSe^- ions with $PhCH_2Br$. $CH_3S^-Na^+$ (0.814 g, 11.6 mmol), Se (0.909 g, 11.5 mmol), $PhCH_2Br$ (1.40 cm^3, 11.5 mmol). The composition of the mixture of products (1.97 g): CH_3SSeCH_2Ph (29%), $(PhCH_2)_2Se_2$ (57%), $(CH_3S)_2$ (14%), was determined from δ_H (s, 2H) and δ_H (s, 3H); $(CH_3S)_2$ and $(PhCH_2)_2Se_2$ were identified by the use of commercial samples which were added to the synthesized mixture. Volatile $(CH_3S)_2$ was assumed to have been greatly reduced in the course of the solvent evaporation. The disproportionation level of CH_3SSeCH_2Ph ($\simeq$80%) was thus calculated by reference to the only $(PhCH_2)_2Se_2$ proportion. $(PhCH_2)_2Se$, which gave no ^{1}H NMR signal, was detected in the mass spectra as a result of the known selenium extrusion from benzylic diselenide under thermal conditions.[19] CH_3SSeCH_2Ph: δ_H 2.24$_5$ (s, 3H), 4.08 (s, 2H); m/z 218 (^{80}Se, M^+, 4%), 91 (100), 65(16) and 39 (9). $(PhCH_2)_2S_2$: δ_H 3.80 (s, 4H); m/z 342 (^{80}Se, M^+, 2%), 91 (100). $(CH_3S)_2$: δ_H 2.39$_5$ (6H, s; m/z 96 ($M^+ + 2$, 11), 94 (M^+, 100%). $(PhCH_2)_2Se$: m/z 262 (^{80}Se, M^+, 7%), 91 (100).

Reaction of $PhSSe^-$ with CH_3I. PhS^-Li^+ in THF (11 cm^3, 11 mmol), Se (0.792 g, 10.0 mmol), CH_3I (0.80 cm^3, 12.8 mmol). The products were identified both by ^{1}H NMR with the use of commercial samples of $(PhS)_2$, $(CH_3Se)_2$ and $PhSCH_3$ compounds, and by GC-MS. The composition of the mixture (1.79 g): $PhSSeCH_3$ (32%), $(PhS)_2$ (35%), $(CH_3Se)_2$ (22%) and $PhSCH_3$ (11%, close to the initial ratio PhS^-:$PhSSe^-$ = 1:10), was determined by combining the integrals of δ_H (s, 3H) with those of aromatic δ_H, $(PhS)_2$ (4 H*o*) and $PhSSeCH_3$ (2H*o*). It was in good agreement with the integration of the GC peaks. Here again, the disproportionation of $PhSSeCH_3$ ($\simeq$70%) was evaluated from the respective proportions of $PhSSeCH_3$ and $(PhS)_2$ in the mixture. $PhSSeCH_3$: δ_H 2.46 (s, 3H), 7.51 (1H*o*, Ar), 7.55 (1H*o*, Ar); m/z 204 (^{80}Se, M^+, 87%), 189 (57), 109 (100), 77 (51), 69 (37), 65 (76), 51 (43), 39 (49). $(PhS)_2$: δ_H 7.45 (2H*o*, Ar), 7.49 (2H*o*, Ar); m/z 218 (M^+, 76%). $(CH_3Se)_2$: δ_H 2.67$_5$ (s, 6H); m/z 190 (^{80}Se, M^+, 88%). $PhSCH_3$: δ_H 2.44$_7$ (s, 3H); m/z 124 (M^+, 100%).

References

1 A. Ahrika, J. Robert, M. Anouti and J. Paris, *New J. Chem.*, 2001, **25**, 741.
2 A. Ahrika and J. Paris, *New J. Chem.*, 1999, **23**, 1177.
3 G. Bosser, M. Anouti and J. Paris, *J. Chem. Soc., Perkin Trans. 2*, 1996, 1993.
4 C. Köllemann, D. Obendorf and F. Sladsky, *Phosphorus Sulfur Relat. Elem.*, 1988, **38**, 69.
5 A. Ahrika, J. Auger and J. Paris, *New J. Chem.*, 1999, **23**, 679.
6 M. Benaïchouche, G. Bosser, J. Paris, J. Auger and V. Plichon, *J. Chem. Soc., Perkin Trans. 2*, 1990, 31.
7 E. Block, in *Dietary Phytochemicals in Cancer Prevention and Treatment*, Plenum Press, New York, 1996, pp. 155–169 and references cited therein.
8 C. Ip and D. J. Lisk, in *Dietary Phytochemicals in Cancer Prevention and Treatment*, Plenum Press, New York, 1996, pp. 179–187.
9 X.-J. Cai, P. C. Uden, E. Block, X. Zhang, B. D. Quimby and J. J. Sullivan, *J. Agric. Food Chem.*, 1994, **42**, 2081.
10 (*a*) H. Rheinbolt and E. Giesbrecht, *Liebigs Ann. Chem.*, 1950, 198; (*b*) H. H. Sisler and N. K. Kotia, *J. Org. Chem.*, 1971, **36**, 1700; (*c*) J. L. Kice and T. W. S. Lee, *J. Am. Chem. Soc.*, 1978, **100**, 5094; (*d*) M. Yoshida, T. Cho and M. Kobayashi, *Chem. Lett.*, 1984, 1109.
11 (*a*) W. Mc Farlane, *J. Chem. Soc. (A)*, 1969, 913; (*b*) V. A. Potapov, S. V. Amosova, P. A. Petrov, L. S. Romanenko and V. V. Keiko, *Sulfur Lett.*, 1992, **15**, 121.
12 F. Gaillard and E. Levillain, *J. Electroanal. Chem.*, 1995, **398**, 77 and references cited therein.

13 G. Bosser and J. Paris, *New J. Chem.*, 1995, **19**, 391.
14 K. W. Sharp and W. H. Koelher, *Inorg. Chem.*, 1977, **16**, 2258.
15 (*a*) C. Degrand, *J. Chem. Soc., Chem. Commun.*, 1986, 1113; (*b*) C. Degrand and R. Prest, *J. Org. Chem.*, 1990, **55**, 5242.
16 (*a*) F. Magno, G. Bontempelli and G. Pilloni, *J. Electroanal. Chem.*, 1971, **30**, 375; (*b*) M. Liu, S.-J. Visco and L. C. De Jonghe, *J. Electrochem. Soc.*, 1989, **136**, 2570.
17 J. Paris and V. Plichon, *Electrochim. Acta*, 1981, **26**, 1823.
18 H. Eggert, O. Nielsen and L. Henriksen, *J. Am. Chem. Soc.*, 1986, **108**, 1725.
19 (*a*) M. A. Lardon, *Ann. N.Y. Acad. Sci.*, 1972, **192**, 132; (*b*) J. Y. Chu and J. W. Lewicki, *J. Org. Chem.*, 1977, **42**, 2491.